Supporting Information for

Porous Coordination Polymer with Reactive Diiron Paddlewheel Unit

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Synthesis of [Fe₂(1,4-BDC)₂(dabco)]·4DMF, 1⊃DMF

All chemicals and deoxidized solvents used in the synthesis were purchased from commercial vendors and used without further purification. All manipulations, unless stated otherwise, were performed under an Ar atmosphere in an Ar-filled glove box or using standard Schlenk techniques. Anhydrous FeCl₂ (0.6 mmol), 1,4-benzenedicarboxylic acid (0.6 mmol) and dabco (1.95 mmol) were mixed in methanol (3 mL) and *N*,*N*-dimethylformamide (27 mL). The solution mixture was reacted at 373 K in glass vial for 48 hours to obtain crystalline product of 1 \supset DMF. The yield of 1 \supset DMF is 80% based on FeCl₂. 1 \supset DMF was characterized by single X-ray diffraction. Powder product for physical measurements was isolated, washed with *N*,*N*-dimethylformamide and dried under Ar.

Crystal structure analysis and other physical measurements

Single crystal X-ray diffraction measurement were performed at 223 K under N₂ flowon a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF/VariMax rotating-anode X-ray generator with confocal monochromated MoKα radiation. Data were processed by a direct method (SIR97) and refined by full-matrix least-squares refinement using the SHELXL-97 computer program. 1⊃DMF crystallizes in the space group *I4/mcm*. The crystal structure contains the unique Fe1 atom which lies on the four-fold axis. The unique N1 atom of dabco also locates on the four-fold axis. DMF and dabco moieties were found to be disorder, and their thermal parameters were refined isotropically. Carbonyl oxygen atom of DMF moiety was modeled in two positions with 50% occupancies. dabco moiety was rotational disordered on the crystallographic four-fold axis and its carbon atom was modeled in three positions and refined using a riding model. We note that hydrogen atoms of carbonyl groups of DMF and dabco ligands were not located in the crystal structure because of their strong disordering, but included in the formula and employed the formula for other studies. The deposited numbers on Cambridge

Crystallographic Data Centre (CCDC) is 950086. X-ray powder diffraction (XRPD) data were collected under air on a Rigaku RINT 2200 Ultima diffractometer with CuK α anode. Thermogravimetric analysis (TGA) was measured using a Rigaku TG8120 under flowing nitrogen with 10 K min⁻¹ ramp rate. The infrared (IR) Spectroscopy was obtained under air using a Nicolet ID5 ATR operating at ambient temperature. Gas adsorption isotherms were measured by BELSORP-mini with either a liquid nitrogen dewar. Analysis tubes for gas adsorption were filled with Ar during preparation to prevent air contaminant. ⁵⁷Fe Mössbauer spectroscopy was performed under dynamic vacuum by using a ⁵⁷Co source with a nominal activity of 1.85 GBq. Velocity scale was calibrated as isomer shifts relative to α -Fe foil. Initial parameters for the least-square fitting of 1 obtained from fitted parameters of the air-exposed sample of 1 measured at same temperature.



Fig. S1. Colors of 1⊃DMF handled under (a) inert Ar atmosphere and (b) air.



Fig. S2. Powder X-ray diffraction patterns of 1: simulated from X-ray crystal structure of $1 \supset DMF$ (black line), and as observed for $1 \supset DMF$ (blue line) and 1 (red line).



Fig. S3. TG profiles of 1⊃DMF (black line) and 1 (red line).



Fig. S4. IR spectra of 1 \supset DMF (blue line) and 1 (red line).



Fig. S5. Mössbauer spectrum of the air-exposed sample of 1 measured at 77 K under dynamic vacuum.



Fig. S6. Mössbauer spectra measured at 150 K under dynamic vacuum of 1 and the air-exposed sample of 1.



Fig. S7. O_2 sorption isotherms at 77 K of 1 before (black profiles) and after (pink profiles) O_2 exposure.

Table. S1. Parameters of Mossbauer spectra measured at 77 K of 1 and the air-exposed sample of 1. Ratios (%) are calculated by the area of each spectrum.

Compound	Spin state	Ratio (%)	<i>I.S.</i> (mm/s)	Q.S. (mm/s)
1	Fe(II) HS	91.6	1.25	2.72
	Fe(III) HS	8.4	0.56	0.90
air-exposed of 1	Fe(II) HS	7.6	1.30	2.86
	Fe(III) HS	92.4	0.56	0.90

Table. S2. Parameters of Mossbauer spectra measured at 150 K of 1 and the air-exposed sample of 1. Ratios (%) are calculated by the area of each spectrum.

Compound	Spin state	Ratio (%)	<i>I.S.</i> (mm/s)	Q.S. (mm/s)
1	Fe(II) HS	86.3	1.22	2.49
	Fe(III) HS	13.7	0.53	0.88
air-exposed of 1	Fe(II) HS	7.8	1.22	2.77
	Fe(III) HS	92.2	0.53	0.88